

REC'D 13 JAN 2005

WIPO

PCT

Europäisches  
Patentamt

European  
Patent Office

Office européen  
des brevets



IB/2004/052886

Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-  
gen stimmen mit der  
ursprünglich eingereichten  
Fassung der auf dem näch-  
sten Blatt bezeichneten  
europäischen Patentanmel-  
dung überein.

The attached documents  
are exact copies of the  
European patent application  
described on the following  
page, as originally filed.

Les documents fixés à  
cette attestation sont  
conformes à la version  
initialement déposée de  
la demande de brevet  
européen spécifiée à la  
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

04102397.9 ✓

**PRIORITY  
DOCUMENT**  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

R C van Dijk

BEST AVAILABLE COPY



Anmeldung Nr:

Application no.: 04102397.9 ✓

Demande no:

Anmeldetag:

Date of filing: 28.05.04 ✓

Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Koninklijke Philips Electronics N.V.  
Groenewoudseweg 1  
5621 BA Eindhoven  
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:

(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.

If no title is shown please refer to the description.

Si aucun titre n'est indiqué se référer à la description.)

Removable pellicle for immersion lithography

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)  
revendiquée(s)

Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/  
Classification internationale des brevets:

G03F7/004

Am Anmeldetag benannte Vertragsstaaten/Contracting states designated at date of  
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL  
PL PT RO SE SI SK TR LI

## Removable pellicle for immersion lithography

This invention relates to methods and materials for radiating a surface immersed in a fluid especially radiating with ultraviolet, deep ultraviolet or vacuum ultraviolet radiation, to materials and methods of patterning a resist layer, to methods of removing such layers, to blanks for patterning, and to products made by such methods and to apparatus for carrying out such methods.

Is known to produce or process smaller features on substrates by irradiating through a fine mask or steering a focused beam for example. Examples of products made using such processes can include semiconductor integrated circuits and optical devices such as high density optical storage discs. A number of problems arise as the feature size is reduced to achieve integration of more components or features on a given size of substrate. For example the wavelength of the electromagnetic radiation may limit the feature size, and fine particles of dust can cause critical defects.

It is known from US patent 5610683 to immerse the substrate in a fluid having a higher refractive index than air and apply a pattern to the substrate lithographically. This can improve the depth of focus and effectively reduce the minimum feature size. It is acknowledged in later US patent 5900354 that immersion optics had been avoided for semiconductor lithography and inspection for four reasons.

Bubbles at the fluid/resist interface can scatter light and cause shadows which cause defects.

It can be hard to remove all traces of the fluid.

The fluid can carry contaminants or can otherwise damage existing features.

Process steps to counter the first three problems can add process complexity and cost. US patent 5900354 suggests using a super critical fluid.

It is also known from EP 1075672 to address the problem of unwanted particle deposition onto masks and wafers during conventional non-immersion lithography. It is mentioned that masks can be coated with a protective membrane of silicon, although it is suggested that such membranes are not suitable for advanced lithography using high energy

radiation of photons, electrons ions or atoms, and suggests instead using thermophoresis to avoid such deposition.

This document also mentions that surface defects can be related to particulate matter being deposited onto surfaces of reticles (masks) and wafer substrates during the various operations required to produce integrated circuits. It indicates that the need to maintain these surfaces substantially free of particulate matter has long been recognized in the microelectronics industry and various schemes to do so have been proposed, such as those set forth in U.S. patents 5,373,806 and 5,472,550. The former discloses the use of thermal energy, such as the use of radiant energy, RF, or resistance heating, to substantially eliminate electrostatic attraction as a mechanism for particle transport and deposition during gas phase processing while the latter describes the use of the photophoretic effect to capture particles by projecting a laser beam inside the processing chamber along a trajectory that does not contact the substrate surface.

The concern about printable defects caused by particle deposition onto surfaces is said to be of particular importance for the next generation of lithographies, including proximity x-ray lithography, direct-write and projection electron-beam lithography (SCALPEL), direct-write and projection ion-beam lithography, and extreme ultraviolet (radiation having a wavelength in the region of 3.5-15 nm) lithography (EUVL) which must provide for exclusion of particles with diameters greater than 0.01  $\mu\text{m}$ . Because of the importance of protecting lithographic surfaces, such as reticles, from deposition of particulate matter for next generation lithographies alternative protection schemes such as clean encapsulation of the exposure chamber, protective gas blankets, and in-situ cleaning of mask surfaces have been investigated. However, each of these alternative schemes has disadvantages and none have been developed successfully.

It is an object of the invention to provide improved materials and processes or apparatus for lithography.

According to a first aspect, the invention provides a method of irradiating a surface immersed in a fluid with a radiation source, the method comprising:

- applying a removable transparent layer to the surface,
- projecting radiation onto the surface through the immersion fluid and through the transparent layer, and subsequently removing the transparent layer.

The thickness of the removable transparent layer is preferably such that certain imperfections in the fluid are out of focus as projected onto the surface. It is estimated that the total required thickness of the removable transparent layer should be such that the Strehl Ratio is not less than 95%. The Strehl ratio indicates the difference between intensity of an ideal and a disturbed Point Spread Function (PSF) The disturbed PSF is caused by a particle or bubble. A critical situation is when the particle or bubble is as close as possible to the substrate to be processed, for example when the particle or bubble is touching the surface of the removable transparent layer. The thickness of the removable transparent layer is 200 nm or greater, e.g. 500nm or greater, 1 micron or greater or 5 micron or greater. The required thickness well depend upon the expected size of the particles or bubbles as well as the optical characteristics of the optical system. Typically the immersion medium, whether gas or liquid, has an index of refraction at the wavelength of the radiation source which is higher than that of air/vacuum. For most practical purposes this is a liquid, preferably water.

An advantage of the transparent layer is that it helps distance certain imperfections from the focus of the radiation on the surface and so can reduce or eliminate shadowing. Hence, the irradiation can be more complete, and defects reduced. It can be particularly effective for imperfections in the form of particles or small bubbles in the immersion fluid, e.g. at the fluid/surface interface. Bubbles can originate from the liquid itself or may be produced by gas escaping from a solid layer or adsorbed thereon. Larger bubbles or particles are rarer and can be dealt with in other ways. The radiation can be for any purpose including inspection, processing, patterning and so on. The immersion fluid can be any fluid including high refractive index liquids or gases.

Additional features which can form dependent claims include the surface comprising a photosensitive layer such as a resist layer, and the projecting comprising projecting a pattern onto the photosensitive layer, e.g. to pattern the resist layer. Such photosensitive layers e.g. resist layers can be particularly sensitive to defects and in many cases a single defect can ruin the entire substrate. 4. The patterned resist layer can be used as a mask in a further lithographic step, e.g. to pattern an underlying layer such as a semiconductor, conducting or insulating layer.

Another such additional feature is the removal of the transparent layer preceding or being combined with a step of developing the resist layer.

The transparent layer can be removed by any suitable chemical or mechanical method or, for example, by a heat treatment step. Mechanical methods of removing the transparent layer can be by cleavage. Chemical methods include wet or drying etching.

Combinations of chemical and mechanical methods can be used, e.g. Chemical Mechanical Polishing. A particularly preferred method is the transparent layer being partly or completely dissolved by a fluid, which could be the same fluid as is used for developing the resist. This can make the process easier since no additional removal step is needed. Properties of the transparent layer may be changed by incidence of radiation and/or by heat treatment. The solubility of the transparent layer may be altered after the immersion in the immersion fluid. This can be particularly useful if the immersion fluid and the developer are both water based for example. The radiation used to change the solubility properties preferably has a different wavelength than that used to pattern any underlying photosensitive layer(s). For example, another such additional feature is the altering being carried out by a post exposure bake process or that the altering is carried out by a flood exposure at a different wavelength to the actinic radiation used for patterning photosensitive layer(s).

In a preferred embodiment the solubility of the transparent layer is different in a developing solution so that the transparent layer may be removed easily by release or dissolution during the developing step. During the initial immersion step the transparent layer is not dissolved or removed, e.g. when the immersion liquid is water or another liquid such as a non-basic aqueous solution. The development solution may be basic, e.g. in a range of pH of 9 or above, e.g. 13-14, and immersion in this liquid results in release or removal of the protective layer, e.g. by dissolution. The developer can be a basic aqueous solution. Alternatively, the initial immersion liquid may be basic, e.g. of pH 9 or above, e.g. 13-14 and the developer solution may be another liquid, e.g. water or a non-basic aqueous solution. In accordance with specific embodiments there is differential solubility in the initial immersion liquid and the developer solution. It is preferred in this embodiment if the transparent layer is a single layer of transparent material.

Another such additional feature is the transparent layer comprising an upper and a lower layer, the upper layer having an alterable solubility. The use of multiple layers can make it easier to retain existing process steps without modification, for example resist coating through to resist development steps.

Another such additional feature is the lower layer having a filter function to protect the resist layer from the altering step.

Typically the lithographic methods of the present invention will be used in processing of semiconductor or polymeric materials for the manufacture of electronic devices and components such as integrated circuits.

Another aspect of the invention provides a method of patterning a photosensitive layer such as a resist covered by a transparent protective layer, having the steps of projecting a pattern through the transparent protective layer onto the photosensitive layer such as the resist, altering the solubility of the protective layer, and removing the protective layer. The method may include developing the resist before removing the protective layer. This helps show that it is not always essential to include the steps of forming the transparent layer, nor essential that the resist be immersed. The abovementioned additional features can apply to this or other aspects.

Another aspect of the invention provides a method of removing a removable protective layer comprising dissolving or releasing the layer by action of the developing solution so that the transparent layer may be removed easily during the developing step. During the initial immersion step the transparent layer is not dissolved or removed, e.g. when the immersion liquid is water, the development solution may be basic – e.g. in the range of pH from 9 and above, e.g. 13-14, and may result in the protective layer being released or dissolved. Alternatively, the initial immersion liquid may be basic, e.g. of pH 9 or above, e.g. 13-14 and the developer solution may be another liquid, e.g. water, and the protective layer is released or removed, e.g. dissolved by the water. In accordance with specific embodiments use is made in the method of differential solubility in the initial immersion liquid and the developer solution. It is preferred in this embodiment if the transparent layer is a single layer of transparent material.

Another aspect of the invention provides a method of removing a removable protective layer comprising the steps of immersing the layer without dissolving it, altering the solubility of the layer by a flood radiation step, then dissolving the layer. Again this helps to show that it is not always essential to include the steps of forming the transparent layer, or irradiating through the layer or immersing the layer.

Another aspect of the invention provides a blank suitable for patterning, having a photosensitive layer such as a resist layer, and a removable transparent protective layer, the removable protective layer being formed of a material of alterable solubility. Such blanks can be separately tradeable, valuable products and articles of manufacture.

Another aspect provides a product manufactured by any of the above methods. In particular this can encompass an integrated circuit, a mask for creating other products, an optical master disc, and optical discs produced from such a master, for example.

Another aspect provides apparatus arranged to carry out any of the above methods.

Other advantages will be apparent to those skilled in the art, particularly in view of other prior art not known to the inventors. Any of the additional features above may be combined together, or combined with any of the aspects of the invention. How the present invention may be put into effect will now be described with reference to the appended  
5 schematic drawings. Obviously, numerous variations and modifications can be made without departing from the claims of the present invention. Therefore, it should be clearly understood that the form of the present invention is illustrative only and is not intended to limit the scope of the present invention.

10

The features of the invention will be better understood by reference to the accompanying drawings, which illustrate preferred embodiments of the invention. In the drawings:

15

Figs. 1a-1d shows a schematic view of a process illustrating a problem to be addressed,

Figs 2a and 2b show a similar schematic view of an embodiment of the invention,

20

Figs 3 and 4a-4d show another embodiment using a bilayer pellicle with a solubility of the top layer altered during resist exposure, and showing steps in exposing through the pellicle and removing the pellicle,

Figs 5a-5d show another embodiment using a bilayer pellicle with a solubility of the top layer altered by a flood exposure prior to a post exposure bake,

Figs 6a-6d show another embodiment using a bilayer pellicle with a solubility of the top layer altered during a post exposure bake,

25

Figs 7, 8a-8d show another embodiment using a single layer pellicle with a solubility of the top layer altered by a flood exposure prior to a post exposure bake, and

Figs 9a-9d show further embodiments using a single layer pellicle with a solubility of the top layer altered during a post exposure bake.

30

Figs 9e-9h show a further embodiment using a single layer pellicle with a solubility of the top layer being different in developer solution.

Figs. 10-12 show process flows in accordance with embodiments of the present invention.



The present invention will be described with respect to particular embodiments and with reference to certain drawings but the invention is not limited thereto but only by the claims. The drawings described are only schematic and are non-limiting. In the drawings, the size of some of the elements may be exaggerated and not drawn on scale for illustrative purposes. Where the term "comprising" is used in the present description and claims, it does not exclude other elements or steps. Where an indefinite or definite article is used when referring to a singular noun e.g. "a" or "an", "the", this includes a plural of that noun unless something else is specifically stated.

Furthermore, the terms first, second, third and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other sequences than described or illustrated herein.

The present invention will be described mainly with reference to altering the solubility of a transparent protective layer but the present invention is not limited to this method. The transparent layer can be removed by any suitable chemical or mechanical method or, for example, by a heat treatment step. Mechanical methods of removing the transparent layer can be by cleavage. Chemical methods include wet or drying etching. Combinations of chemical and mechanical methods can be used, e.g. Chemical Mechanical Polishing. The particularly preferred method is the transparent layer being partly or completely dissolved by a fluid, which could be the same fluid as is used for developing the resist. This can make the process easier since no additional removal step is needed. Properties of the transparent layer may be changed by incidence of radiation and/or by heat treatment. The solubility of the transparent layer may be altered after the immersion in the immersion fluid. This can be particularly useful if the immersion fluid and the developer are both water based for example. The radiation used to change the solubility properties preferably has a different wavelength than that used to pattern any underlying photosensitive layer(s). For example, a post exposure bake process or a flood exposure at a different wavelength to the actinic radiation used for patterning photosensitive layer(s) may be used to change the solubility characteristics.

Embodiments of the invention will be described in the context of immersion lithography though other applications, other than lithographic patterning, are included within the scope of the present invention, e.g. irradiation for inspection or for other processing steps,

and examples of other types of immersion. For example, the present invention can be used in patterning of microelectronic circuits or mastering of high-density optical discs. Figs 1a-d show for reference a process showing an effect of one of the key concerns in immersion lithography, the formation of defects in the exposed resist pattern as a result of light being scattered from bubbles/particles present in the immersion fluid during exposure. The immersion medium can have an index of refraction at the wavelength of the radiation to be used in the optical system which is higher than that of air/vacuum. For most practical purposes this is a liquid, preferably water.

The wavelength of light typically used for lithography is similar to UVC, i.e. in the range 90 to 280 nm. For particle sizes less than 10% of the wavelength there is little scatter, i.e. less than 1%. Thus, particles or bubbles of the order of 10 nm to 20 nm are probably not significant in many practical applications and equipment. Using a wavelength of 193 nm it has been estimated that a pellicle thickness of 200nm or more is required to guarantee a Strehl ratio above 95% for a bubble of 50nm in conventional lithographic equipment. Similarly, for 100nm bubbles, a pellicle thickness of 1100nm or more is preferred and for a bubble size of 200nm a pellicle thickness of 3400nm or more is preferred. For more advanced methods of computing scattered energies for spherical and other objects which can be used to optimize the thickness of the transparent layer, see "Light Scattering by particles: Computational Methods", P.W. Barber and S. C. Hill, World Scientific, 1990.

In Fig. 1a radiation in the form of light from a source (not shown) is shone down onto a surface exemplified in the form of a photosensitive layer such as a resist layer (layer 2) on a substrate (layer 1). The source of radiation may be visible, infra-red, ultra-violet, e.g. deep ultraviolet (DUV), actinic, or vacuum ultraviolet (VUV) radiation, or other forms of electromagnetic radiation. The photosensitive layer is not limited to a resist layer, e.g. it may also be made of a material such as photosensitive BCB which after development provides a patterned insulating layer, e.g. in the formation of capacitors. In the following reference will be made to resist in the context of examples of application of the invention, however wherever the word "resist" occurs it should be understood that any photosensitive layer is also disclosed and included within the scope of the present invention. The radiation is focused by a lens or other projection system (not shown) to form a pattern of two lines or points on the resist. The substrate is immersed in an immersion fluid (layer 3), so that the radiation, e.g. light passes through the immersion fluid to reach the resist. Fig 1b shows the result after exposure and removal of the immersion fluid. The pattern remains in the resist, and the substrate can proceed to further processing steps (not shown). In figs 1c and 1d, the

effect of a small imperfection in the immersion fluid such as a particle or bubble at the boundary of the immersion layer and the resist layer is shown. This particle creates a shadow on the resist during exposure. The result in Fig. 1d is a defective pattern in the resist which can lead to a defective end product.

5           The proposed solution to this problem is the use of a transparent spacing layer termed an 'immersion pellicle' or optical spacer. The 'immersion pellicle' is designed to ensure that small bubbles/particles, which are present in the immersion fluid, e.g. at the fluid/pellicle interface, are kept sufficiently 'out of focus' during exposure of a surface, e.g. a photosensitive. Larger bubbles or particles which are large enough to shadow the surface are  
10   rarer, and easier to detect and remove by other means such as filtering or heating for example. Figs. 2a and 2b show an example in the context of a process for exposing a pattern on a resist film on a substrate.

          A useful additional feature of this 'immersion pellicle' is that, in addition to providing particle protection to the resist film, it is preferably easily removable after  
15   exposure, but prior to, or during the subsequent development of the resist. This removable 'immersion pellicle' can consist of a single or multiple layers, depending on the properties of the constituent materials and the preferred process flow. However, the total thickness of the pellicle should be sufficient to ensure that any particles that settle on the top surface of the pellicle are sufficiently far from the focal point of the optical system, so as not to impact the  
20   quality of the image projected onto the resist. For example, for a 50nm bubble a pellicle thickness of between 200nm and 1000nm, e.g. between 500 and 1000nm would be sufficient, depending on the projection arrangement of the radiation and its wavelength.

          A number of pellicle designs are possible. It is useful but not essential if the pellicle is designed to be insoluble in the immersion fluid, whilst being soluble in the  
25   developer. In the case of 193nm (and 248nm) lithography both the immersion fluid and developer are water based, thus altering, which includes switching, of the solubility of the pellicle is needed if a separate pellicle removal step is to be avoided. In the following paragraphs several single and bi-layer pellicle embodiments are described, to enable such  
altering.

30           Figs 3 and 4a-4d, EXAMPLE 1,

          This example is notable for the bi-layer pellicle consisting of a developer soluble bottom layer and a photosensitive top layer for which solubility switching is initiated during resist exposure. The developer may be water based. The bottom layer may be water soluble. For this embodiment, the basic materials are commercially available. The bottom

layer may be made of materials used as anti-reflective coatings such as AZ Aquatar, JSR Microelectronics NFC520/NFC640 coatings. Optionally, an adhesive layer may be applied between the bottom layer and the top layer, e.g. a primer such as HMDS or TMSDEA. Processing can be carried out using existing processing equipment, or the existing equipment can be adapted to automate the new steps.

Pellicle Composition for example 1:

A schematic drawing of a structure including the pellicle is shown in Fig. 3. Layer 1 is a substrate, layer 2 is the resist, layer 3 is the immersion fluid, and layers 4 and 5 are the pellicle. The pellicle serves to space apart the resist from the immersion fluid. The pellicle is comprised of two layers; a bottom layer (lift-off material), layer 4 which is soluble in a resist developer solution (independent of exposure) and a photosensitive top protective layer, layer 5, for which solubility switching is initiated during exposure of the resist and completed during the subsequent post exposure bake (PEB). An optional adhesive layer may be applied between the lift-off layer 4 and the photosensitive layer 5.

Process Flow for example 1:

The basic process flow is as follows:

- a. Spin-coat resist layer (not shown) and optional bake step
- b. Spin-coat bottom pellicle layer (not shown) and optional bake step
- c. Spin-coat top pellicle layer (not shown) and optional bake step
- d. Expose resist in scanner (fig 4a)
- e. Post expose bake PEB resist (fig 4b)
- f. Develop resist (fig 4c)

Figs. 4a-4d schematically represents the process flow during exposure and development. The scanner can be any exposure tool such as a scanner, stepper or step-scan tool. The formation of the layers can be carried out by conventional methods such as spin coating or other methods. As such methods of formation are well known, they need not be described further here. During exposure of the water, in addition to exposing selected regions in the resist (layer 2), regions in the pellicle top layer (layer 5) are also exposed (Fig. 4a). Again, such exposure methods and apparatus to project a pattern onto the resist and focus it accurately, are well known and need not be described here in more detail. If this top layer is based on a chemically amplified (CA) resist chemistry, the dissolution characteristics of this top layer will remain unchanged until after the subsequent PEB. As a result of the PEB step, the exposed regions of the top pellicle layer will become soluble in developer solution

(Fig. 4b). Thus during development of the wafer, the exposed regions of the top protective layer will dissolve exposing the soluble bottom pellicle layer and exposed resist to the developer solution, allowing these layers to be developed, and lift-off of the unexposed regions of the top pellicle layer to occur (Fig. 4c). Fig 4d shows the result after lift off, showing the patterned resist, ready for any further process steps (not shown).

An advantage of this process is that all processing between resist coating and development can be carried out in an existing standard lithographic system without modification to the apparatus. In principle the steps of fig 4 and the other figures can be used with other processes, other ways of creating the layers, other types of radiation for other purposes and other post processing steps for example. The pellicle can still serve its purpose without being completely transparent, and in some cases need not be removed, or completely removed. It can comprise more than two layers.

Figs 5a-5d, EXAMPLE 2:

This is similar to example 1 in that a bi-layer pellicle is used. It differs in that the layers consist of a developer soluble bottom layer and photosensitive top layer for which solubility switching is initiated during a flood exposure subsequent to the resist exposure and prior to Post Exposure Bake (PEB). For this approach, the basic materials are commercially available, as indicated above. Processing can be carried out using existing processing equipment, although the process flow does require an additional flood exposure of the wafer to be carried out after the resist exposure, at a wavelength for which:

- a) The top pellicle layer is sensitive and
- b) The bottom pellicle layer is non-transparent or the resist is non-sensitive.

Pellicle Composition for example 2 is similar to example 1:

Layer 1 is a substrate, layer 2 is the resist, layer 3 is the immersion fluid, and layers 4 and 5 are the pellicle, as shown in Fig. 3. The pellicle serves to space apart the resist from the immersion fluid. The pellicle is comprised of two layers; a bottom layer (lift-off ~~material, which is soluble in the resist developer solution~~ (independent of exposure) and a photosensitive top protective layer, for which solubility switching is initiated via a flood exposure of the top pellicle layer. The underlying resist layer is 'shielded' from this flood exposure through the filtering nature of the pellicle bottom layer. An optional adhesive layer may be applied between the lift-off layer 4 and the photosensitive layer 5.

Process Flow for example 2:

The basic process flow is as follows:

- g. Spin-coat resist layer (not shown) and optional bake step

- h. Spin-coat bottom pellicle layer (not shown) and optional bake step
- i. Spin-coat top pellicle layer (not shown) and optional bake step
- j. Expose resist in scanner (fig 5a)
- k. Flood exposure of top pellicle layer (second wavelength, fig 5b)
- 5 l. Post expose bake PEB resist (fig 5c);
- m. Develop resist (fig 5d).

Figs 5a-5d schematically represent the process flow during exposure and development. The scanner can be any exposure tool such as a scanner, stepper or step-scan tool. During exposure of the wafer, in addition to exposing selected regions in the resist (layer 2), regions in the pellicle top layer (layer 5) may also be exposed (Fig. 5a). A subsequent flood exposure at a wavelength for which the top pellicle layer is sensitive and either the bottom pellicle layer is non-transparent, or the resist is insensitive, ensures that the top pellicle layer is fully dissolvable in the resist developer solution (Fig. 5b). If this top layer is based on a chemically amplified (CA) resist chemistry, the dissolution characteristics of this top layer will remain unchanged until after the subsequent PEB. As a result of the PEB step, the top pellicle layer will become soluble in developer solution (Fig. 5c). Thus during development of the wafer, the flood exposed top protective layer will dissolve exposing the soluble bottom pellicle layer and exposed resist to the developer solution, allowing these layers to be developed (Fig. 5d). Again an advantage is that all processing between resist coating and development can be carried out in an existing standard litho track.

#### Figs 6a-6d, EXAMPLE 3:

Again this is similar to example 1 in that a bi-layer pellicle is used. In this case the layers consist of a developer soluble bottom layer and a top layer for which solubility switching is initiated via a post exposure bake PEB. For this approach, the basic materials are commercially available as indicated above. Processing can be carried out using existing processing equipment, or the existing equipment can be modified to automate the new steps.

#### Pellicle Composition for example 3:

Again the structure shown in Fig. 3 is used. The pellicle is comprised of two layers; a bottom layer (lift-off material), which is soluble in the resist developer solution (independent of exposure) and a top protective layer, for which solubility switching is initiated via a post exposure bake. The bottom pellicle layer serves to prevent potential mixing of the top pellicle and resist layer during the spin-coating process. Switching of the solubility of the top pellicle layer should occur at a temperature below that at which

switching occurs for the resist layer. An optional adhesive layer may be applied between the lift-off layer 4 and the top layer 5.

**Process Flow for example 3:**

The basic process flow is as follows:

- 5 n. Spin-coat resist layer (not shown) and optional bake step
- o. Spin-coat bottom pellicle layer (not shown) and optional bake step
- p. Spin-coat top pellicle layer (not shown) and optional bake step
- q. Expose resist in scanner (fig 6a)
- r. Post expose bake PEB resist (fig 6b)
- 10 s. Develop resist (fig 6c)

Figs 6a-6d schematically represent the process flow during exposure and development. The scanner can be any exposure tool such as a scanner, stepper or step-scan tool. During exposure of the wafer, only resist layer is exposed (Figs 6a and 6b). During the subsequent post exposure bake, the solubility of the top (protective) pellicle layer is switched  
15 such that the top pellicle layer is fully dissolvable in the resist developer solution (Fig. 6c). During development of the wafer, the top protective layer will dissolve exposing the soluble bottom pellicle layer and exposed resist to the developer solution, allowing these layers to be developed (Fig. 6d). As before, an advantage is that all processing steps between resist coating and development can be carried out in an existing standard litho track with minor  
20 modifications (addition of flood exposure unit).

**Figs 7, 8a-8d, EXAMPLE 4:**

In this case, a single layer pellicle is used. The pellicle consists of photosensitive material for which solubility switching is initiated during a flood exposure subsequent to the resist exposure and prior to Post Exposure Bake PEB. For this approach,  
25 the basic materials are commercially available as indicated above. Processing can be carried out using existing processing equipment, although the process flow does require an additional flood exposure of the wafer to be carried out after the resist exposure, at a wavelength for which the pellicle layer is sensitive and the resist is non-sensitive. Existing apparatus can be modified to automate the new steps.

**Pellicle Composition for example 4:**

As shown in Fig. 7, layer 1 is a substrate, layer 2 is the resist, layer 3 is the immersion fluid, and layer 4 is the pellicle. The pellicle is comprised of a single layer, for which solubility switching is initiated via a flood exposure of the pellicle layer after exposure on the resist in the scanner. The scanner can be any exposure tool such as a scanner, stepper

or step-scan tool. The underlying resist layer is insensitive to the wavelength at which this flood exposure occurs.

Process Flow for example 4:

The basic process flow is as follows:

- 5 t. Spin-coat resist layer (not shown) and optional bake step
- u. Spin-coat pellicle layer (not shown) and optional bake step
- v. Expose resist in scanner (fig 8a)
- w. Flood exposure of pellicle layer (second wavelength, fig 8b)
- x. Post expose bake PEB resist (fig 8b)
- 10 y. Develop resist (fig 8c)

Figs 8a-8d schematically represent the process flow during exposure and development. The scanner can be any exposure tool such as a scanner, stepper or step-scan tool. During exposure of the wafer, in addition to exposing selected regions in the resist (layer 2), regions in the pellicle layer (layer 4) may also be exposed (Fig. 8a). A subsequent flood exposure at a wavelength for which the top pellicle layer is sensitive and the resist is insensitive ensures that the pellicle layer is fully dissolvable in the resist developer solution (Fig. 8b). If this top layer is based on a chemically amplified (CA) resist chemistry, the dissolution characteristics of this top layer will remain unchanged until after the subsequent PEB. As a result of the PEB step, the top pellicle layer will become soluble in developer solution (Fig. 8c). Thus during development of the wafer, the flood exposed top protective layer will dissolve exposing exposed resist to the developer solution, allowing this layer to be developed (Fig. 8d). Again an advantage is that processing can be carried out using existing processing equipment, although the process flow does require an additional flood exposure of the wafer. Existing apparatus can be modified to automate the new steps.

Figs 9a-9d, EXAMPLE 5:

The pellicle consisting of a material for which solubility switching is initiated during a post exposure bake PEB. For this approach, the basic materials are commercially available as indicated above. Processing can be carried out using existing processing equipment.

Pellicle Composition for example 5:

Pellicle is comprised of a single layer, as shown in Fig. 7, for which solubility switching is initiated via a post exposure bake of the pellicle layer after exposure on the resist in the scanner. The scanner can be any exposure tool such as a scanner, stepper or step-scan



tool. Switching of the solubility of the top pellicle layer should occur at a temperature below that at which switching occurs for the resist layer.

**Process Flow for example 5:**

The basic process flow is as follows:

- 5    z.       Spin-coat resist layer (not shown) and optional bake step
- aa.     Spin-coat pellicle layer (not shown) and optional bake step
- bb.     Expose resist in scanner (fig 9a)
- cc.     Post expose bake PEB resist (fig 9b)
- dd.     Develop resist (fig 9c)

10       Figs 9a-9d schematically represent the process flow during exposure and development. The scanner can be any exposure tool such as a scanner, stepper or step-scan tool.

During exposure of the wafer, only resist layer is exposed (Figs. 9a and 9b). During the subsequent post exposure bake, the solubility of the pellicle layer is switched such  
15    that the pellicle layer is fully dissolvable in the resist developer solution (Fig. 9c). During development of the wafer, the pellicle layer will dissolve exposing the resist to the developer solution, allowing this layers to be developed (Fig. 9d). As before, an advantage is that all processing between resist coating and development can be carried out in an existing standard litho track with minor modifications (addition of flood exposure unit). Existing apparatus can  
20    be modified to automate the new steps.

**EXAMPLE 6:**

According to a further embodiment of the present invention a further single layer pellicle layer and method is provided. The pellicle comprises a material that is designed to exhibit differential release properties in the initial immersion liquid and the developer  
25    solution. For example, the pellicle can be insoluble in water, but soluble in a basic or alkaline solution (e.g. standard developer). The developer solution may be adjusted to have a pH range of 9 or greater, e.g. 13-14. Such materials are available from JSR and TOK, for use as 248 and 193nm top ARC's. Alternatively, the initial liquid may be made basic and the developer solution is water or an aqueous solution having a pH about 7 or lower. In both  
30    cases the pellicle is designed so that it is removable or releasable in the developer solution and not in the initial immersion liquid.

An embodiment of the present invention is a process providing a coating thickness of up to or greater than 500nm. Processing can be carried out using existing

processing equipment. A schematic drawing of this pellicle is shown in Fig 7 however in this embodiment two wavelengths are not required – one is sufficient.

The basic process flow is as follows:

Spin-coat resist layer (not shown) and optional bake step

5 Spin-coat pellicle layer (not shown) and optional bake step

Expose resist in scanner (fig 9e)

Post expose bake PEB resist (fig 9f)

Develop pellicle and resist layers (fig 9g)

10 Fig. 9h schematically represents the process flow during exposure and development. During exposure of the wafer, only resist layer is exposed (Fig. 9e and f).

During development of the wafer, the pellicle layer will dissolve or be released in the developer solution thus exposing the resist to the developer solution, allowing this layer to be developed (Fig. 9g). The final result being shown in Fig. 9h.

15 Suitable materials for the pellicle, each of which is an embodiment of the present invention, can be:

a) Polyvinyl alcohol which is soluble in water but not in a basic solution. In this case the developer solution would be water or a non-basic aqueous solution.

b) Polyvinylphenol which is soluble in a basic solution but not in water or a non-basic aqueous solution.

20 c) Polymethacrylic acid which is soluble in a basic solution but not in water or a non-basic aqueous solution.

In the embodiments b) and c) the developer would be a basic solution and the initial immersion liquid would be water or a non-basic aqueous solution.

25 A suitable developer would be based tetramethylammonium hydroxide (TMAH). A suitable solution would contain 2 to 3% tetramethylammonium hydroxide (CAS No. 75-59-2) and water (CAS No. 7732-18-5) 97-98%. The pH range is generally in the range 13-14.

Figs 10-12, process overviews

30 Fig. 10 shows an overview of a process according to an embodiment. In step 10, a transparent layer is applied to a surface. At step 12, radiation is projected through the transparent layer to focus on the surface. At step 14 the transparent layer is removed. This set of steps can be applied to a wide variety of applications. Fig 11 shows an overview of a process according to another embodiment. At step 16, a pattern is projected onto a resist layer though a transparent layer on the resist. At step 18, the solubility of the transparent layer is

altered. At step 20, the resist is developed and the transparent layer is removed, by dissolving. In Fig 12, a surface having a protective layer is immersed at step 22. At step 24, the solubility of the protective layer is altered by light or other radiation. At step 26, the protective layer is dissolved. Again these sets of steps can be applied to a wide variety of applications.

As described above, a method of irradiating to pattern a photosensitive layer such as a resist (layers 1,2) immersed in a fluid (layer 3), involves applying a removable transparent layer (layer 4 or 4 and 5), projecting the radiation onto the photosensitive layer through the immersion fluid and through the transparent layer, such that imperfections in the fluid are out of focus as projected on the surface, and subsequently removing the transparent layer. The transparent layer can help distance such imperfections from the focus of the radiation on the surface and so can reduce or eliminate shadowing. Hence the irradiation can be more complete, and defects reduced. It can be particularly effective for imperfections in the form of small bubbles in the immersion fluid, e.g. at the fluid/surface interface. The radiation can be for any purpose including inspection, processing, patterning and so on. The removal of the transparent layer can be carried out by any suitable method, e.g. mechanical, chemical or heat treatment and may be combined with a step of developing an underlying photosensitive layer such as a resist layer. Other variations can be envisaged which are intended to be within the scope of the claims.

## CLAIMS:

1. A method of irradiating a surface (layers 1 and 2) comprising a photosensitive layer and immersed in an immersion fluid (layer 3), the method comprising:
  - applying a removable transparent layer (layer 4, or layers 4 and 5) to the surface,
  - 5 - projecting electromagnetic radiation onto the surface through the immersion fluid and through the transparent layer, and
  - subsequently removing the transparent layer.
2. The method of claim 1, wherein the projecting comprises projecting a pattern  
10 onto the photosensitive layer.
3. The method of claim 2, wherein the photosensitive layer is a resist layer and the projecting comprises projecting a pattern to pattern the resist layer.
- 15 4. The method of claim 3, further comprising a step of using the patterned resist layer as a mask in a further lithographic step.
5. The method according to claim 1, wherein the thickness of the removable transparent layer is such that imperfections in the immersion fluid are out of focus as  
20 projected on the surface.
6. The method of claim 2, wherein the step of the removal of the transparent layer precedes or is combined with a step of developing the photosensitive layer.
- 25 7. The method of claim 1, the transparent layer being removed by dissolving with a dissolving fluid.
8. The method according to claim 7, wherein the dissolving fluid is used for developing the photosensitive layer.

9. The method of claim 1 comprising a step of altering the solubility of the transparent layer after the immersion in the immersion fluid.

5 10. The method of claim 9, the altering being carried out by a post exposure bake process.

11. The method of claim 9, the altering being carried out by a flood exposure at a different wavelength to the wavelength of the radiation.

10

12. The method of claim 1, the transparent layer comprising an upper and a lower layer, the upper layer having an alterable solubility.

13. The method of claim 12, the lower layer having a filter function to protect the  
15 resist layer from the altering step.

14. A method of patterning a photosensitive layer covered by a transparent protective layer, the method comprising:

- 20
- projecting a pattern through the transparent protective layer onto the photosensitive layer,
  - altering the solubility of the protective layer, and
  - removing the protective layer with a solvent.

15. The method of claim 14, wherein the photosensitive layer is a resist, further  
25 comprising the step of developing the resist.

16. A method of removing a removable protective layer comprising the steps of immersing the layer without dissolving it, altering the solubility of the layer by a flood radiation step, then dissolving the layer.

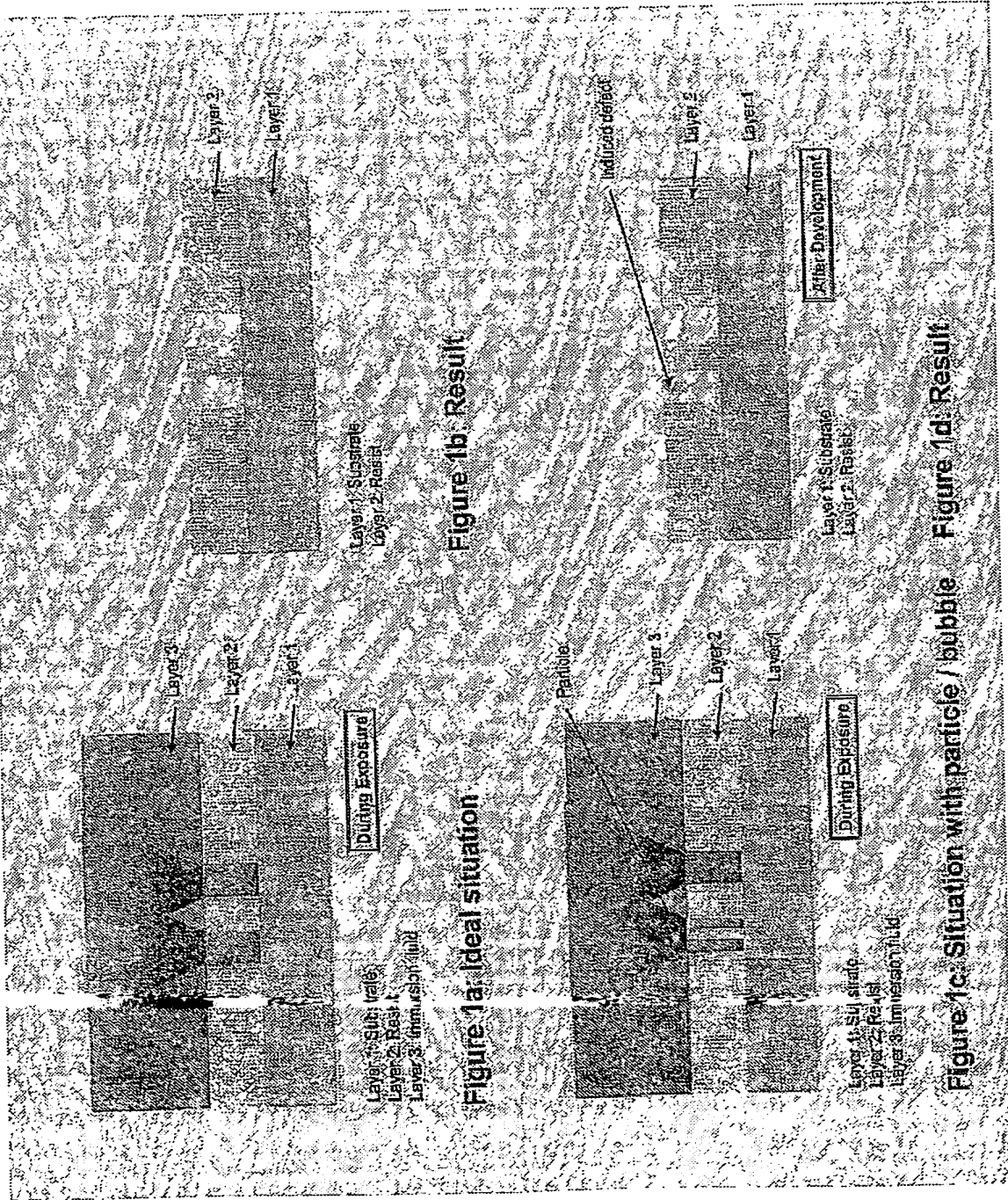
30

17. A blank suitable for patterning, having a photosensitive layer, and a removable transparent protective layer, the removable protective layer being formed of a material of alterable solubility.

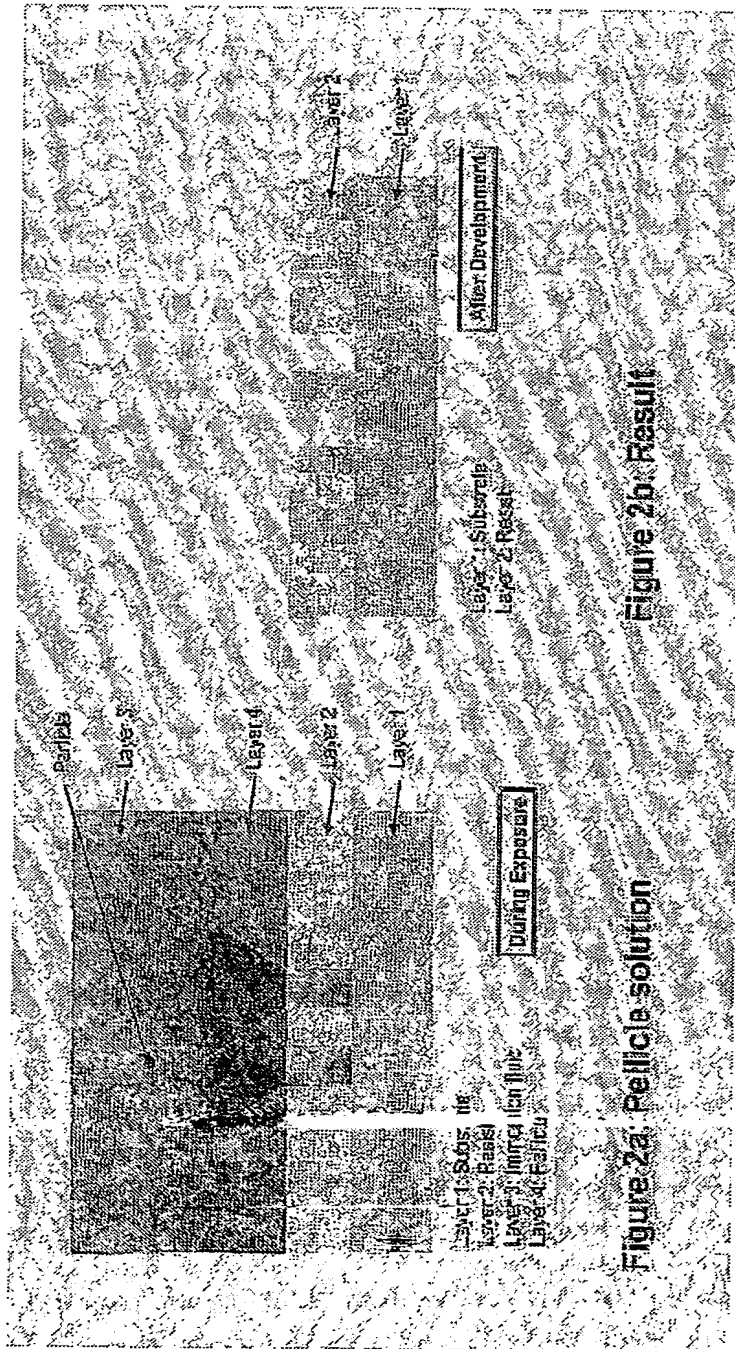
## ABSTRACT:

A method of irradiating to pattern a photosensitive layer such as a resist (layers 1,2) immersed in a fluid (layer 3), involves applying a removable transparent layer (layer 4 or 4 and 5), projecting the radiation onto the resist through the immersion fluid and through the transparent layer, such that imperfections in the fluid are out of focus as projected on the surface, and subsequently removing the transparent layer. The transparent layer can help distance such imperfections from the focus of the radiation on the surface and so can reduce or eliminate shadowing. Hence the irradiation can be more complete, and defects reduced. It can be particularly effective for imperfections in the form of small bubbles or particles in the immersion fluid especially at the fluid/surface interface for example. The radiation can be for any purpose including inspection, processing, patterning and so on. The removal of the transparent layer can be combined with a step of developing the resist layer.

Fig. 4a

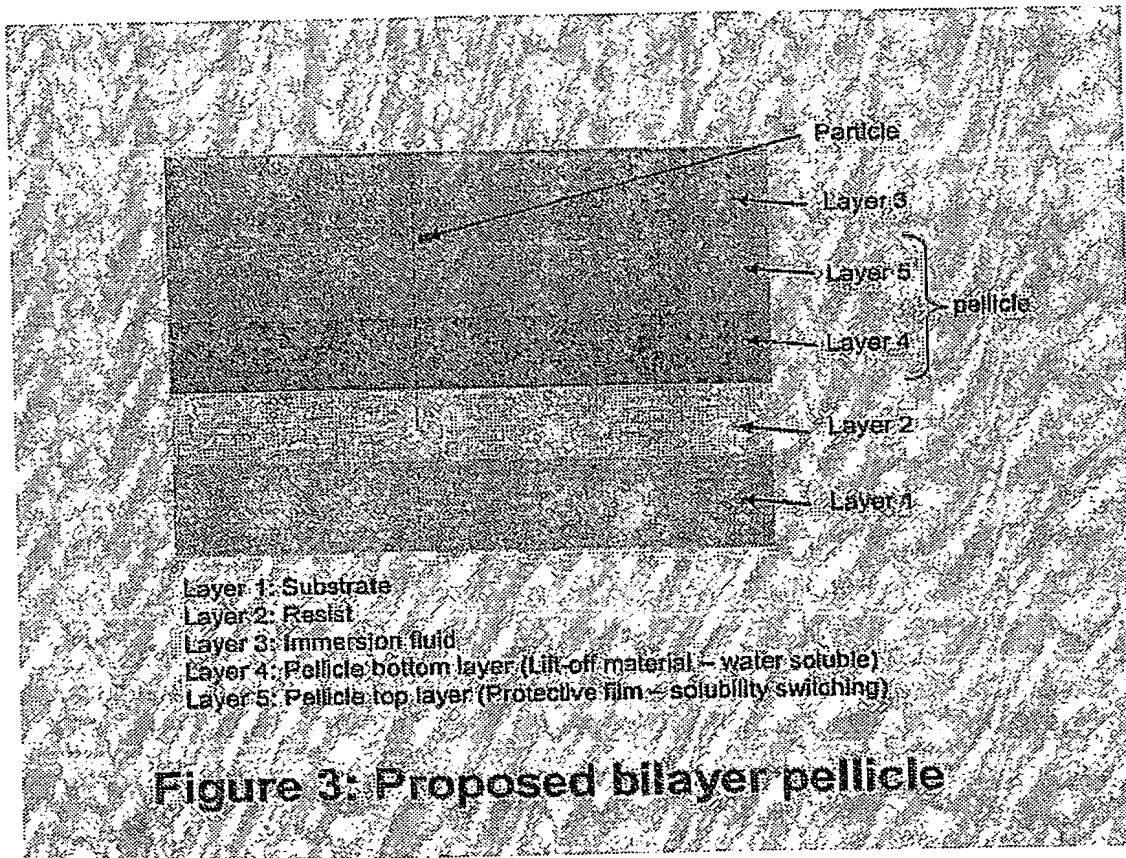


2/11

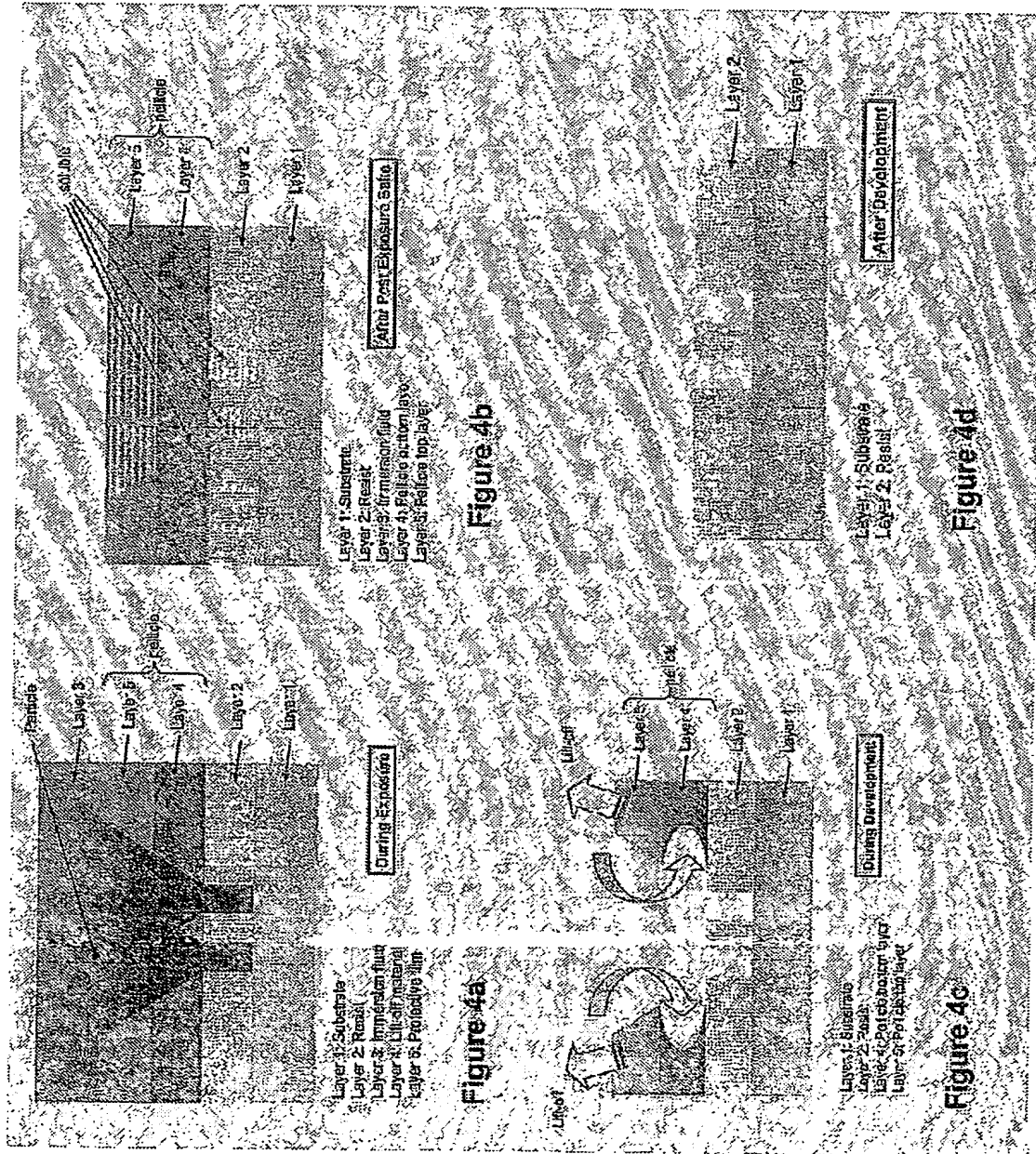




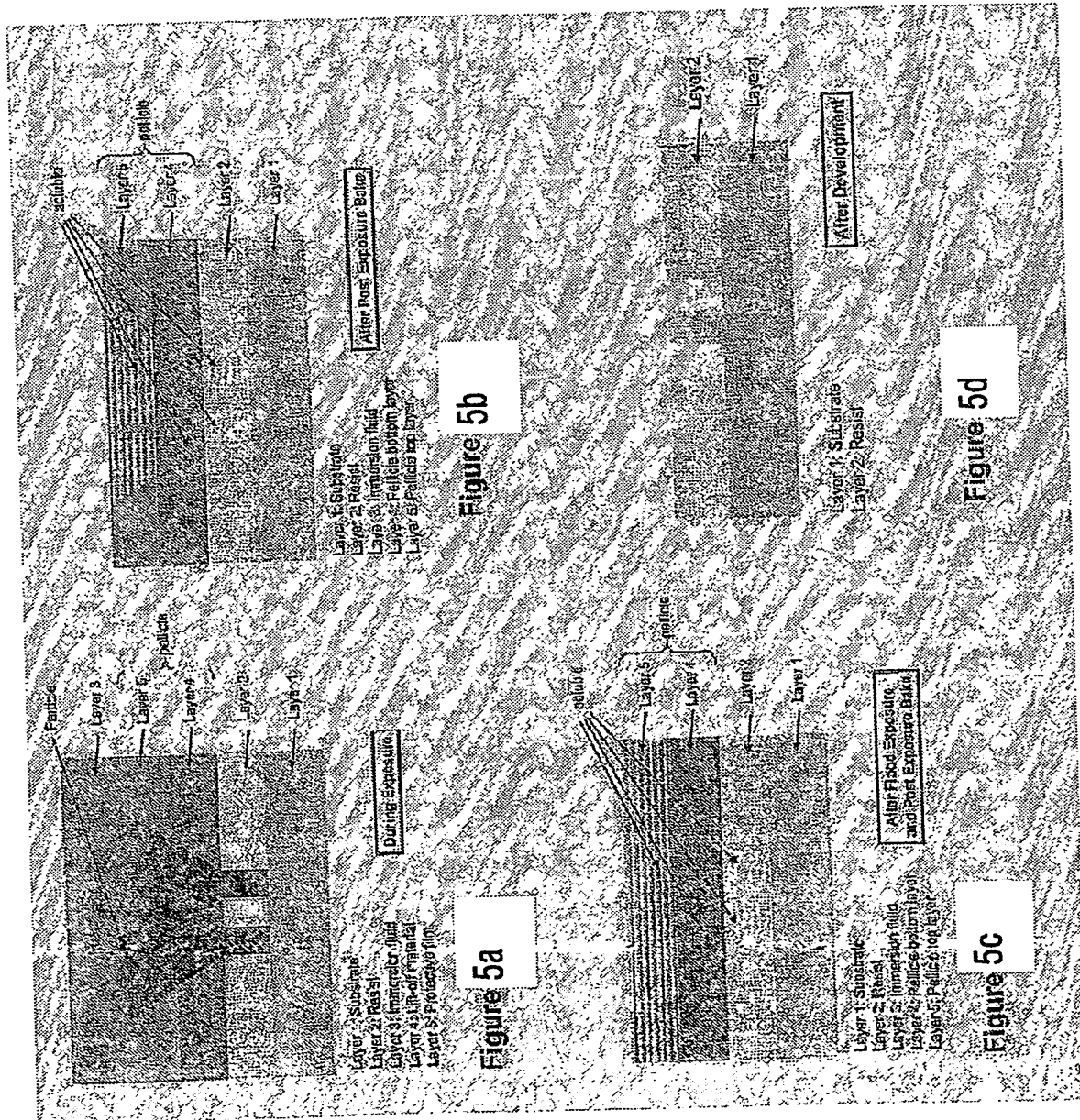
3/11



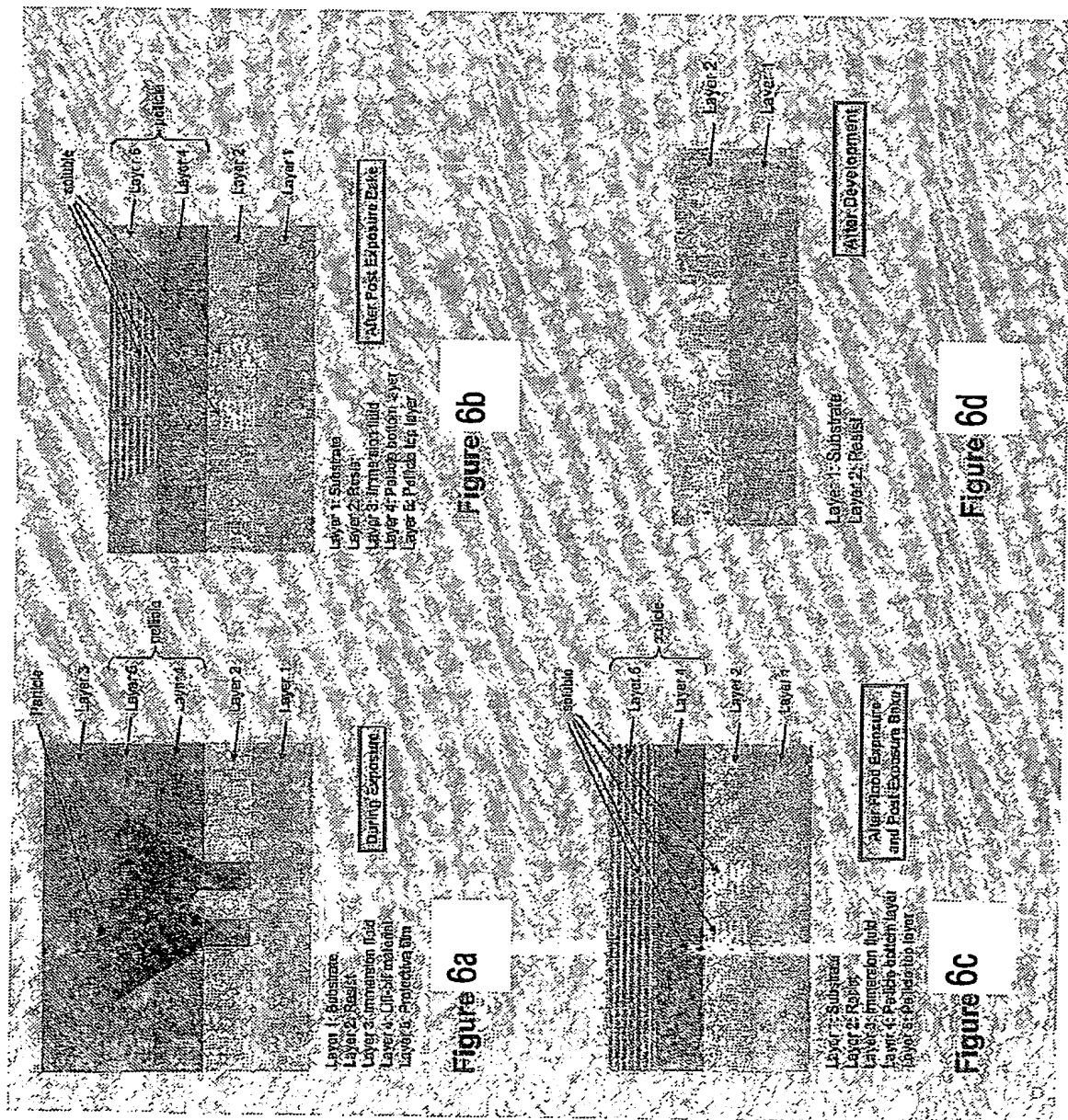
4/11



5/11

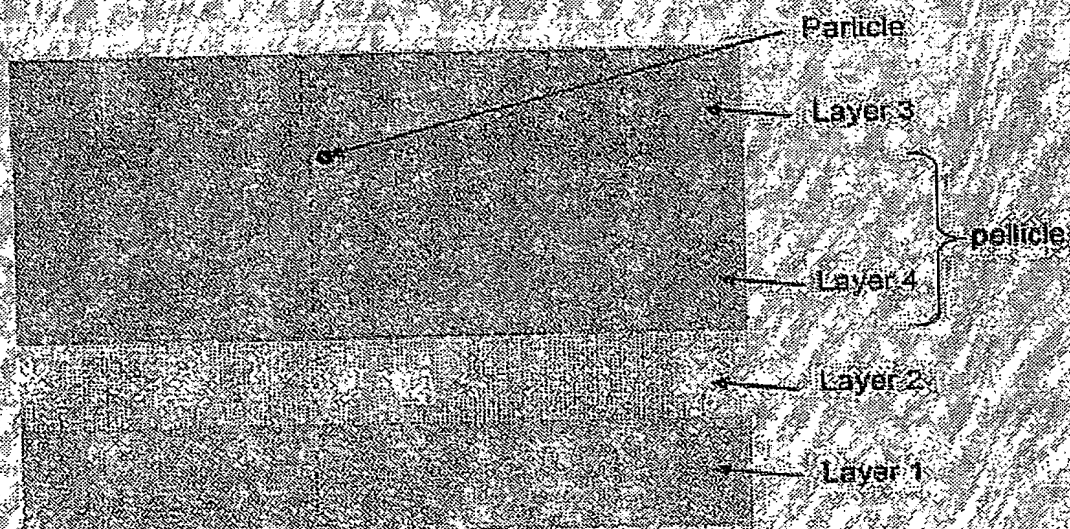


6/11





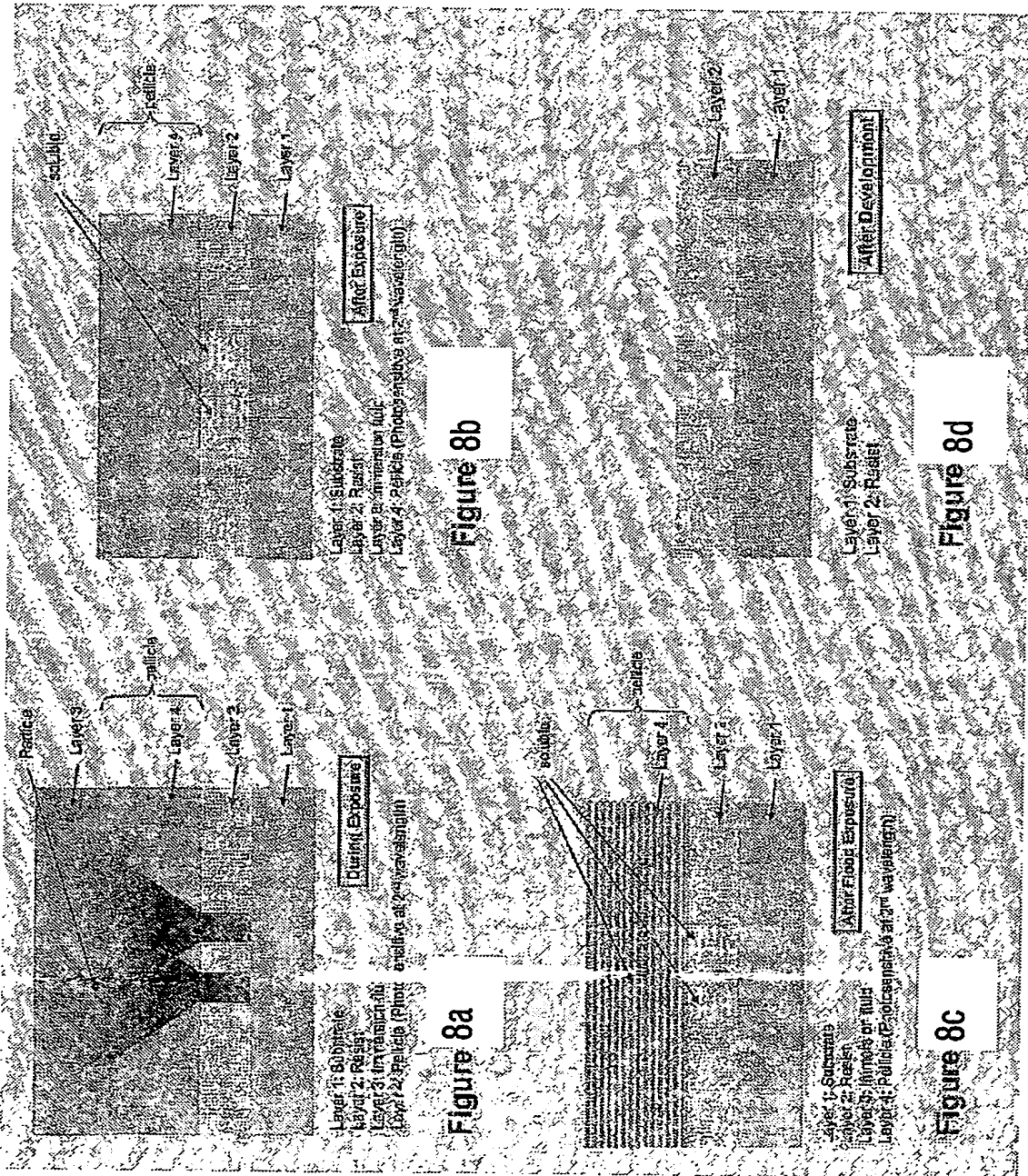
7/11



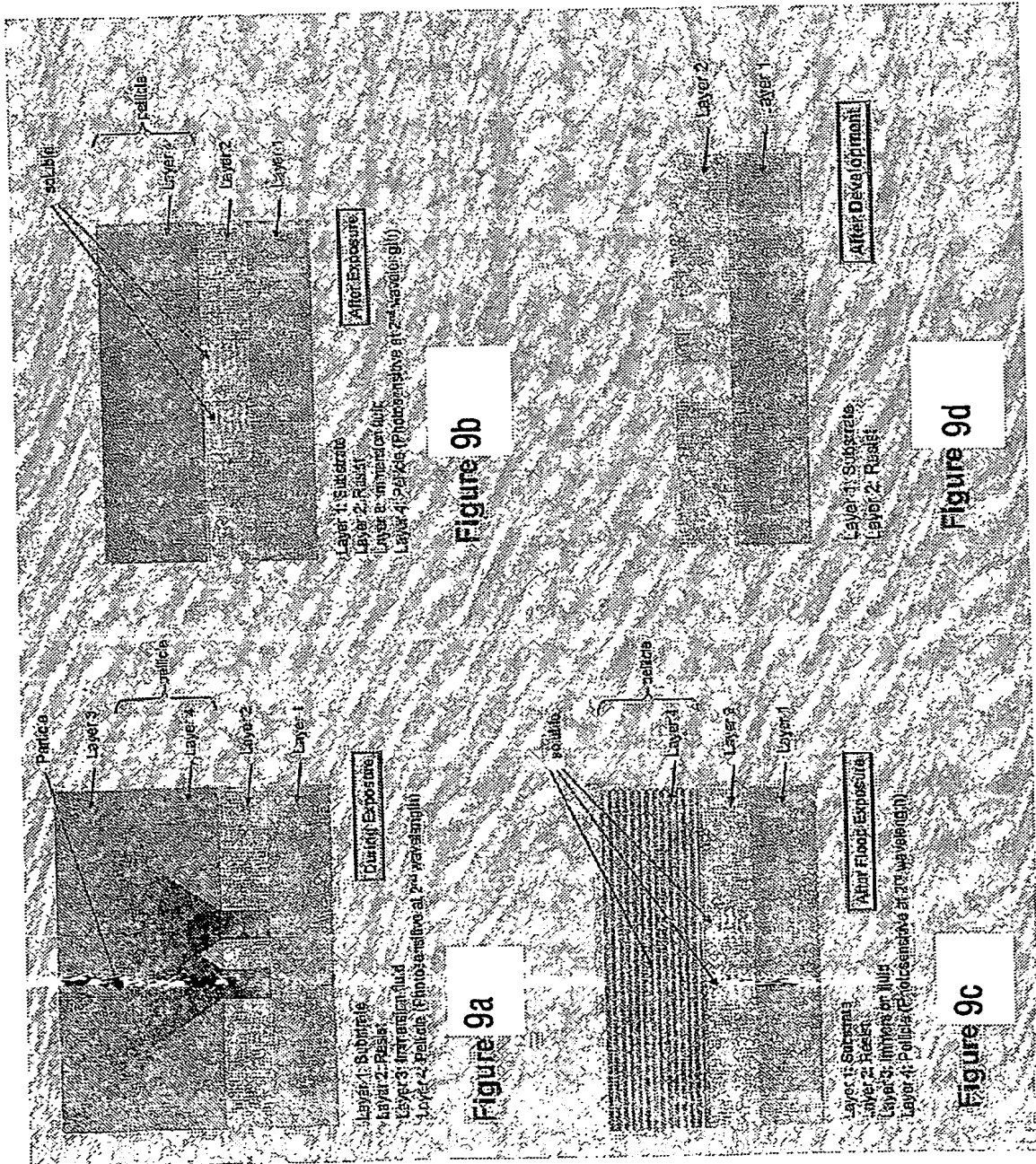
Layer 1: Substrate  
Layer 2: Resist  
Layer 3: Immersion fluid  
Layer 4: Pellicle (Photosensitive at 2<sup>nd</sup> wavelength)

**Figure 7** Proposed single layer pellicle

8/11



9/11



10/11

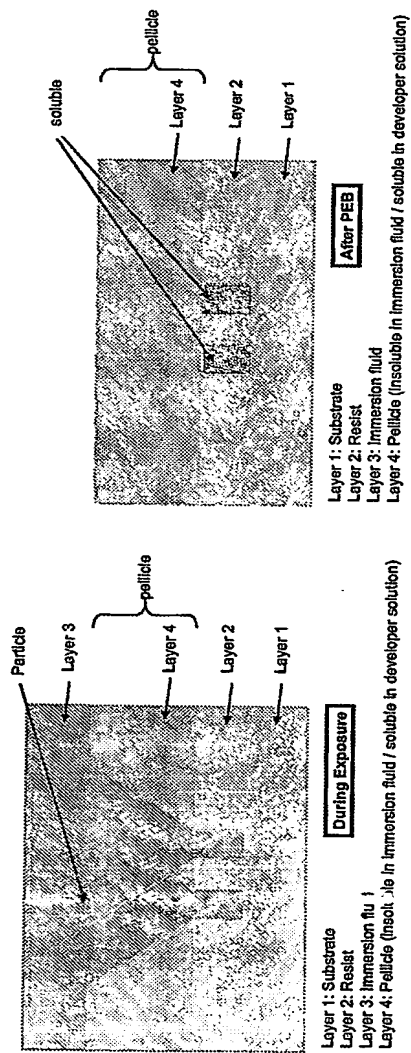


Figure 9e

Figure 9f

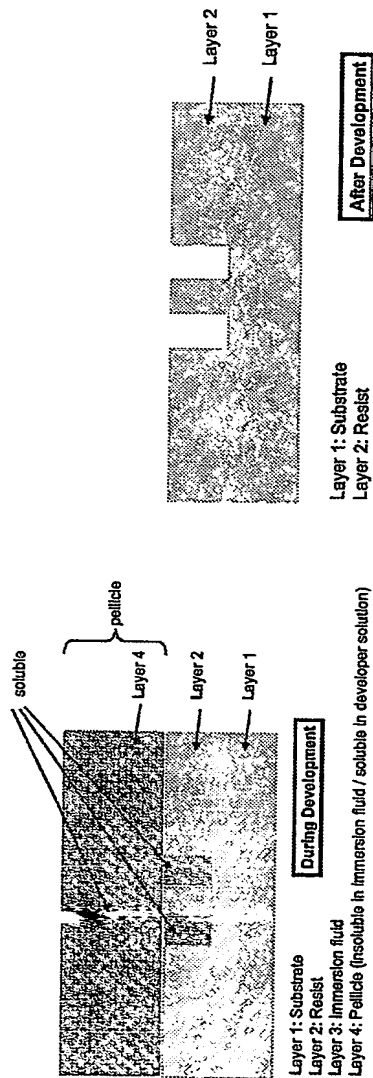


Figure 9g

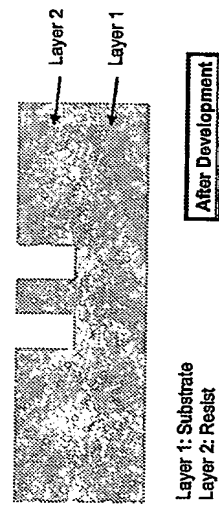


Figure 9h



11/11

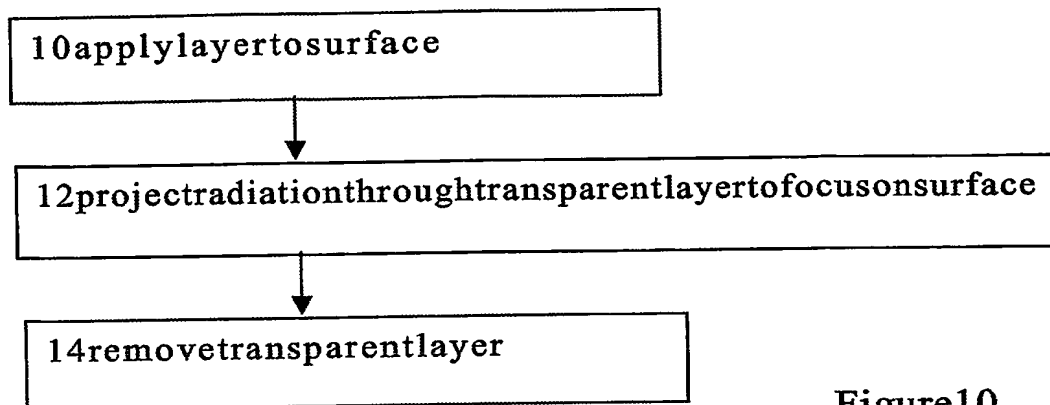


Figure 10

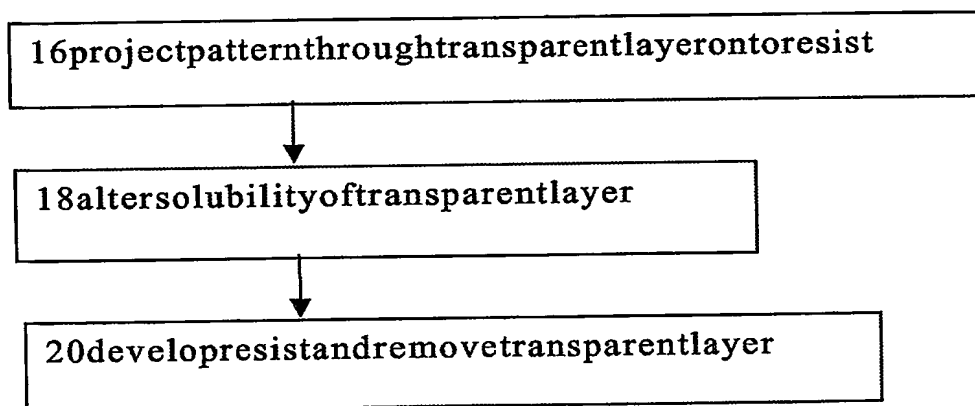


Figure 11

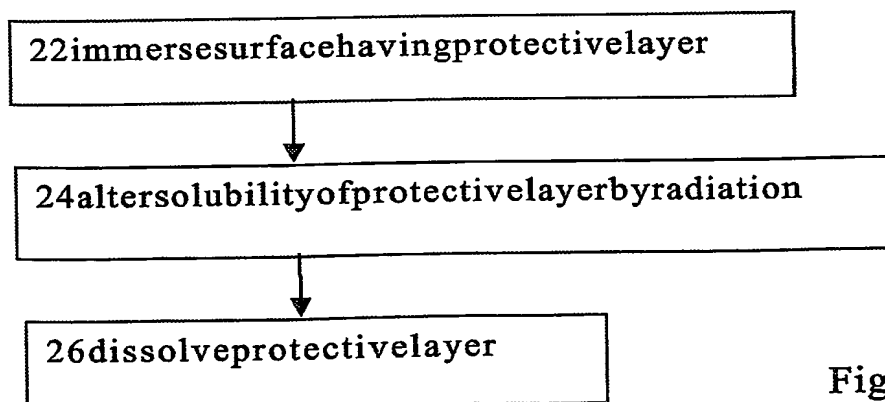


Figure 12

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**